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CONTINUOUS ELECTRODEIONISATION: MODULE DESIGN CONSIDERATIONS FOR THE PRODUCTION OF HIGH PURITY WATER

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1   ELECTRODEIONISATION

Electrodeionisation (EDI) is a process that removes ionisable species from liquids using electrically active media and an electrical potential to influence ion transport. The electrically active media in EDI devices may function to alternately collect and discharge ionisable species, or to facilitate the transport of ions continuously by ionic or electronic substitution mechanisms. EDI devices may comprise media of permanent or temporary charge, and may be operated batchwise, intermittently, or continuously. EDI devices may be operated to cause electrochemical reactions specifically designed to achieve or enhance performance, and may comprise electrically active membranes such as semipermeable ion exchange or bipolar membranes. The *continuous electrodeionisation* (CEDI) process, a subset of EDI, is distinguished from the EDI collection/discharge processes such as *electrochemical ion exchange* (EIX) or *capacitive deionisation* (CapDI), in that the ionic transport properties of the active media in CEDI are a primary sizing parameter, as opposed to ionic capacity. CEDI devices typically comprise semi-permeable ion exchange membranes and permanently charged media such as ion exchange resin. The CEDI process is sometimes also referred to as *filled-cell electrodialysis*.

1.1   Continuous Electrodeionisation (CEDI)

A typical CEDI device comprises alternating semipermeable anion and cation ion exchange membranes. The spaces between the membranes are configured to create liquid flow compartments with inlets and outlets. A transverse DC electrical field is imposed by an external power source using electrodes at the bounds of the membranes and compartments. When subjecting the compartments to an electric field, ions in the liquid are attracted to their respective counterelectrodes. The result is that the compartment bounded by the anion membrane facing the anode and the cation membrane facing the cathode becomes ionically depleted and the compartments bounded by the anion membrane facing the cathode and cation membrane facing the anode becomes ionically concentrated. The space within the ion depleting compartments, and in some cases in the ion concentrating compartments, is filled with electrically active media. The ion exchange media enhances the transport of ions and can also participate as a substrate for controlled electrochemical reactions. Different media configurations are possible, such as intimately mixed anion and cation exchange resins (mixed bed or MB) or separate

sections of ion exchange resin, each section substantially comprised of resins of the same polarity: e.g., either anion or cation resin (layered bed or LB and single bed or SB).

1.2 Mechanisms of Ion Removal

There are two distinct operating regimes for CEDI devices: enhanced transfer and electroregeneration. In the enhanced transfer regime, the resins within the device remain in the salt forms. In low conductivity solutions, the ion exchange resin is orders of magnitude more conductive than the solution, and act as a medium for transport of ions across the compartments to the surface of the ion exchange membranes. The second operating regime for CEDI devices is known as the electroregeneration regime. This regime is characterised by the continuous regeneration of resins by electrically produced hydrogen and hydroxide ions. "Regenerating" the resins to their H^+ and OH^- forms allows CEDI devices to remove weakly ionised compounds such as carbonic and silicic acids, and to remove weakly ionised organic compounds.

2   CONTINUOUS ELECTRODEIONISATION - MIXED BED (CEDI-MB)

Electrodeionisation has been studied since the mid-1950's[1-4], but it was first commercialised in 1987 by a division of Millipore Corporation that is now part of Vivendi Water[5]. The first commercial CEDI devices used mixed-bed ion exchange resin as a conductive media in the diluting compartments, as shown in Figure 1.
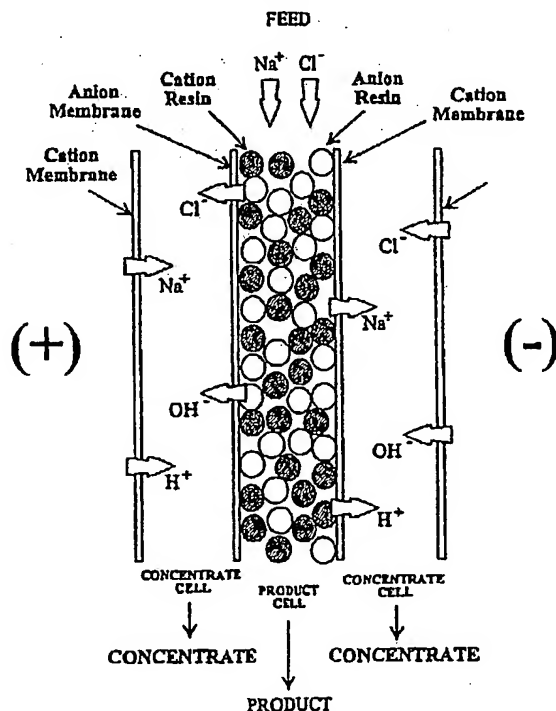

Figure 1 *Process diagram for CEDI-MB device*
Resin filler in product compartments only

This is presently the most commonly used type of electrodeionisation device, with over 1000 installations worldwide. Most commercially available CEDI modules are plate

and frame devices with multiple arrangements of alternating diluting and concentrating compartments between a set of electrodes, hydraulically in parallel and electrically in series. This configuration allows construction of modules capable of flow rates as high as 18 m^3/h. In most cases, CEDI has been used for purification of water that has been pretreated by reverse osmosis (RO), where the RO is performing the roughing demineralisation and the CEDI is functioning as a polisher. However, CEDI-MB devices can provide over 95% salt removal on feeds with up to 500 ppm TDS.

2.1   CEDI-MB: Intermembrane Spacing

For devices using a mixed-bed resin filler, one of the most important design constraints is the distance between the ion exchange membranes[6]. In order for the resin to transport an ion, there must be a continuous path of the appropriate type of ion exchange resin, i.e. all cation resin for transfer of cations and all anion resin for transfer of anions. For simple cubic packing and equal quantities of equal diameter anion and cation beads, the probability (*P*) of a direct conductive path can be related to the number of resin beads (*N*) between the membranes by Equation 1:

$$P = \frac{(N+1)}{2^N} \tag{1}$$

The effect of intermembrane spacing on salt removal in a CEDI-MB device has also been demonstrated experimentally, as shown in Table 1.

Cell thickness, mm	Salt removal, %	Product µS/cm
1.0	99.8	1.2
2.3	99.9	0.6
4.7	94.3	34
7.2	71.7	170

Table 1   *Relationship between cell thickness and performance for a CEDI-MB device (Feed solution NaCl, 600 µS/cm, 25°C. Constant velocity, 0.86 cm/sec)*

The experimental results show the optimum intermembrane spacing to be about 2.3 mm, and most commercial devices use a spacing of 2.5–3.0 mm. This represents approximately three resin beads between the membranes.

2.2   CEDI-MB: Resin Packing

It has also been shown that the performance of a CEDI-MB device can be improved significantly by the use of uniform particle size ion exchange resins instead of conventional resins, which have a broad distribution of bead sizes[7]. The uniform beads allow a higher packing density, approaching a hexagonal close-packed structure. The effect of packing density on salt removal is illustrated by the data in Table 2.

Feed, μS/cm	Product Megohm-cm, Non-uniform beads	Product Megohm-cm, Uniform beads
145	0.4	0.7
87	0.8	1.5
65	1.5	4.2
41	3.4	10.5

Table 2   *Relationship between resin particle size distribution and performance for a CEDI-MB device*

2.3   CEDI-MB: Optimisation of Electroregeneration

Membrane/resin combinations must be carefully chosen to selectively catalyse the electrochemical splitting of water at various locations within the CEDI device. The dissociation of water preferentially occurs at bipolar interfaces in the ion-depleting compartment where localised conditions of low solute concentrations are most likely to occur. The two primary types of interfaces in CEDI devices are resin/resin and resin/membrane. For CDI-MB, water splitting at both types results in effective resin regeneration. The selection of resins for electrodeionisation is derived from the need for different reactivity, mechanical and transfer properties based on the conditions of operation and contaminants to be removed[8]. What works best for chemically regenerated mixed-bed ion exchange is not necessarily optimum for CEDI.

In addition to proper selection of resin, the electroregeneration process can be enhanced by several methods that reduce the electrical resistance of the cell and therefore allow greater passage of DC current. The first means of accomplishing this was to increase the water recovery and therefore the amount of salt in the concentrate compartments. This is generally done by incorporating a feed-and-bleed arrangement using a pump to recirculate the concentrate stream and ensure adequate flow distribution while decreasing the flow rate of the bleed that is sent to drain.

An alternative method of reducing the cell resistance is to inject a conductive salt such as NaCl into the feed to the concentrate compartments using a dosing pump. There are several possible drawbacks to this method. Increasing the TDS may prevent reclaiming the concentrate stream for other uses, and may increase the possibility of salt bridging and stray DC currents. If the concentrate is used to feed the electrode compartment, this can also lead to generation of chlorine gas at the anode.

A third, and preferred method, is to incorporate a resin filler into the concentrate compartments, as shown in Figure 2. This eliminates the need for injection of a conductive salt. It has also been seen that the resin helps ions transfer away from the surface of the concentrate side of the ion exchange membrane. This reduces the ion concentration in the boundary layer, reducing the driving force for back-diffusion and improving salt removal.
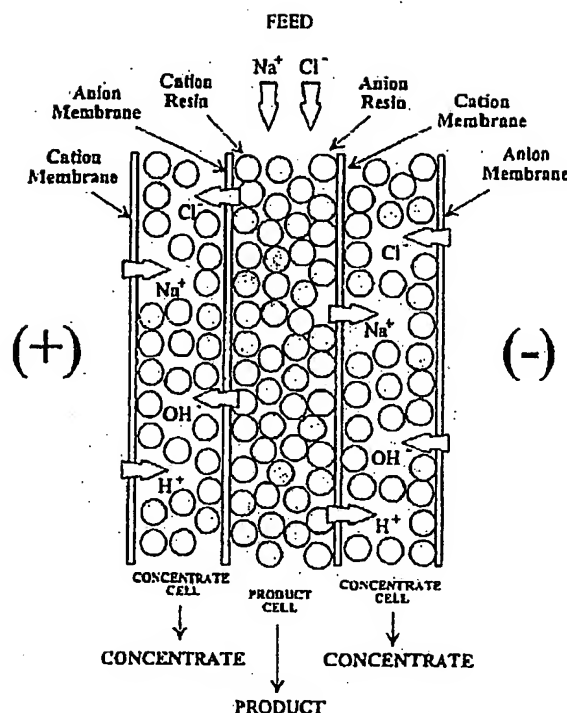
FEED

Figure 2   *Process diagram for CEDI-MB device*
Resin filler in product & concentrate compartments

3   CONTINUOUS ELECTRODEIONISATION - LAYERED BED (CEDI-LB)

Figure 3 depicts the electrodiaresis (EDR or CEDI-LB) process[9]. The schematic is much the same as Figure 2 except that the media comprise separate, sometimes alternating layers (or in one variation, clusters) of ion exchange resin, each layer substantially comprised of resins of the same polarity: e.g., each layer either anion or cation resin. Liquid to be deionised flows sequentially through the layers of resins. As with CEDI-MB devices, the ion exchange resin or resins can also be added to the ion concentrating compartments to enhance ionic transport.

For CEDI-LB devices there is essentially no "enhanced transfer" regime and less limitation on the intermembrane spacing. This is because transfer of only one polarity ion is enhanced at any given time. Construction of resin-filled devices is somewhat easier with thicker resin compartments, and 10 mm cells are often used for CEDI-LB devices. One of the main design constraints is the selection of ion exchange resin, which must catalyse the water splitting reaction. Resin selection must also take into account the relative electrical resistance and selectivity of the layers, so that the DC current is distributed as desired, depending upon the performance objectives[10]. Thus the resin properties of importance for CEDI-LB can be much different than for CEDI-MB.

The use of thicker cells also reduces the amount of ion exchange membrane used to construct the device, which reduces the cost. However, operation at a higher flow per unit membrane area compromises the performance for salt removal, as shown in Figure 4. The CEDI-LB performance is more sensitive to increases in feed water concentration and to decreases in feed water temperature.
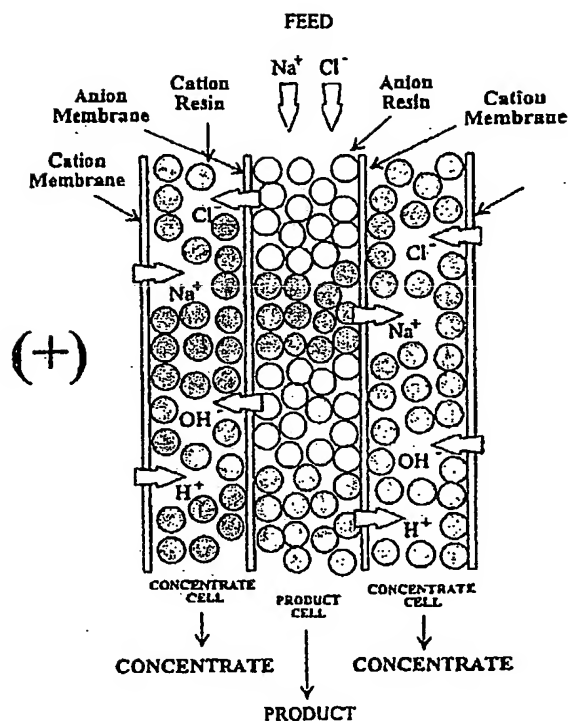
Figure 3 *Process diagram for CEDI-LB device*
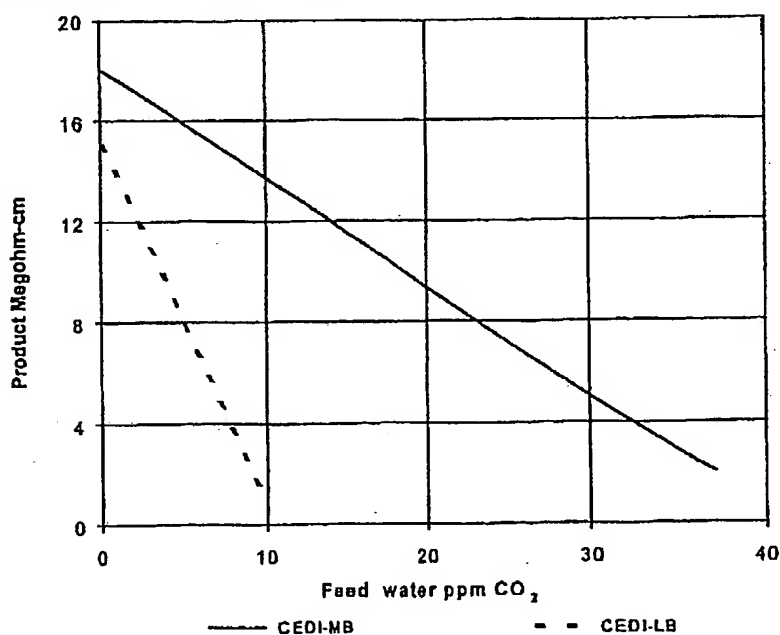*Layered resin in product compartments only*

Figure 4 *Effect of feed water ionic loading on performance of CEDI-MB and CEDI-LB devices at 10°C*

4 CONTINUOUS ELECTRODEIONISATION - SEPARATE BED (CEDI-SB)

Another electrodeionisation device[11] uses separate resin compartments, with the cation exchange resin placed in a compartment between a cation membrane and the anode, with the resin in direct contact with the electrode. The anion exchange resin is between an

anion membrane and the cathode. The two ion exchange membranes create a concentrate compartment at the center of the cell. This configuration is shown in Figure 5.
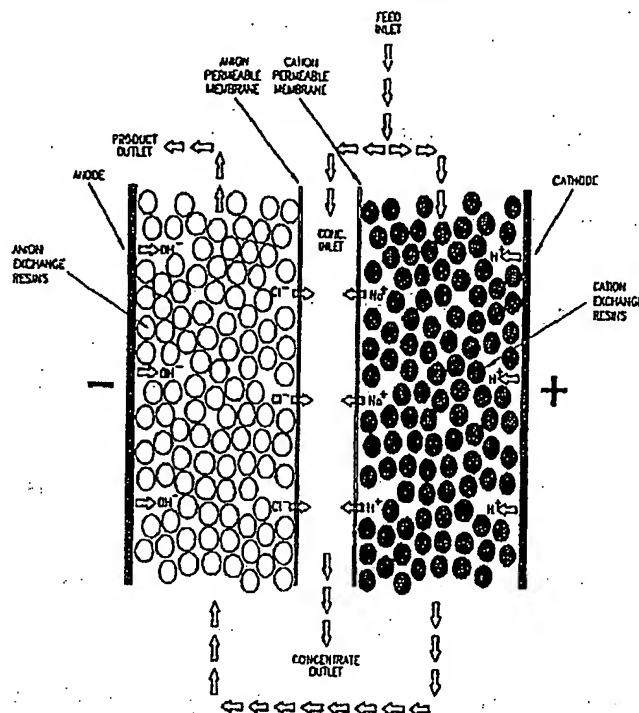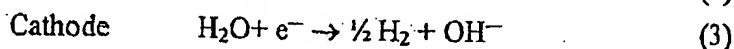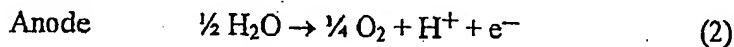

Figure 5 *Process diagram for CEDI-SB device*
          Resin in electrode compartments only

Instead of splitting water at a resin/membrane or resin/resin interface, this process obtains the hydrogen or hydroxyl ions needed to regenerate the resin from the electrode reactions shown in Equations 2 and 3.

$$\text{Anode} \qquad \tfrac{1}{2}\,H_2O \rightarrow \tfrac{1}{4}\,O_2 + H^+ + e^- \qquad\qquad (2)$$

$$\text{Cathode} \qquad H_2O + e^- \rightarrow \tfrac{1}{2}\,H_2 + OH^- \qquad\qquad (3)$$

There is an additional reaction that occurs at the anode, resulting in the formation of free chlorine:

$$Cl^- \rightarrow \tfrac{1}{2}\,Cl_2 + e^- \qquad\qquad (4)$$

Since the resins are in the electrode compartments, the O_2, H_2, and Cl_2 gas that is created remains in the product water, and requires an additional gas removal process step. It is possible that the electrode reaction could produce enough chlorine to reduce the life of the ion exchange resin.

Thate has presented results comparing the performance of a CEDI-SB device with a CEDI-MB device[12], but these results are misleading because both devices were constructed with 10 mm intermembrane spacing, which is not appropriate for a MB device. Figure 6 compares Thate's results for a 10 mm CEDI-SB device with a 2.5 mm CEDI-MB device. In this case the performance of the CEDI-MB is seen to be much better than the CEDI-SB, which is the opposite of the results obtained with both 10 mm devices.

The main disadvantage of the CEDI-SB device is that it requires a set of electrodes for each cell, which is only cost effective for low flow rate applications where a single cell

is sufficient. There have been some attempts to produce a multi-cell device using bipolar ion exchange membranes, but these have not been commercialised due to the short life of the bipolar membranes.
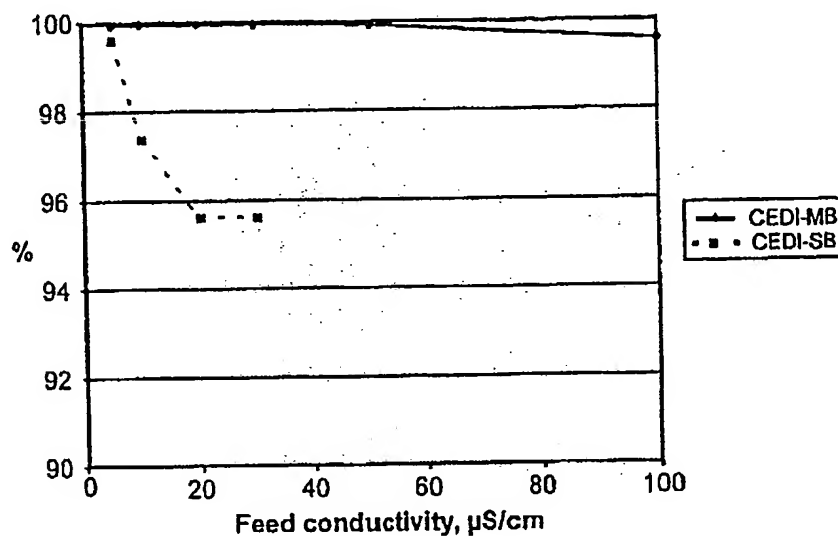

Figure 6 *Comparison of CEDI-MB and CEDI-SB devices (% conductivity removal)*

5 SUMMARY

There are two general classes of CEDI devices, those using true mixed-bed resin which require intermembrane spacing of 2.5–3 mm, and those using layered or separate ion exchange resin beds with 10 mm intermembrane spacing. The thin cell CEDI-MB devices provide the best salt removal, while the thick cell CEDI-LB units are less costly to fabricate, and the thick cell CEDI-SB primarily for low flow rate applications. Selection of the ion exchange resin filler is critical to CEDI device performance.

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